

# THE PRINCIPAL MAGNETIC SUSCEPTIBILITIES OF SINGLE CRYSTALS OF RARE EARTH SALTS AT LOW TEMPERATURES. PART II. PRASEODYMIUM SALTS

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**ABSTRACT.** The principal susceptibilities of praseodymium salts have been measured from room temperature down to liquid air temperature. The results are discussed in terms of the crystalline electric field theory. It is found that (1) on the basis of a single suitable cubic field the observed magnetic moment at all temperatures in the range studied can be explained satisfactorily. (2) The observed large anisotropies of the crystals point to the existence of strongly asymmetric rhombic field. (3) a rough estimate of the rhombic part of the field shows that the splitting by it is by no means small and compares favourably with the cubic splitting. (4) The  $\chi_1$ -axis of praseodymium sulphate rotates by about 63 degrees in the range studied.

## INTRODUCTION

Following Van Vleck (1932), Penney and Schlapp (1932) if one attributes all the observed deviations in the magnetic properties of the rare earth ion,  $\text{Pr}^{+3}$  from the ideal free ion behaviour, to the splitting of the energy levels of the  $\text{Pr}^{+3}$  ion, under the influence of strong and generally asymmetric crystalline fields, one should expect the mean of the three principal susceptibilities to be determined almost wholly by the cubic part of the field. The rhombic part will have very little effect on the mean of the three susceptibilities though the individual susceptibilities will be affected considerably. This conclusion has been verified satisfactorily in the case of cerium salts (Mookherji, 1949).

Though in most of the crystals the crystalline fields are predominantly cubic in symmetry, the small deviations from the cubic part of the field produce nearly as great an effect on the susceptibilities as cubic parts. On the other hand if we consider the mean of the three principal susceptibilities of the crystal, which is the one measured with crystal powder, the effect of the non-cubic part is not so conspicuous, owing to averaging out of the effect along the three principal axes, which are not all of the same sign (Mookherji 1946; Bose, 1948). The measurements on powder will reveal only the effects of the cubic part of the field whereas measurement with single crystal can reveal the effects of both the cubic and the non-cubic part. That is why measurements on the principal susceptibilities of single crystals

are much more informative than the usual measurements, namely, on the crystal powder.

It is true that the axes of the crystal fields associated with the different paramagnetic ions in crystals will not in general be parallel to one another and even in an anisotropic crystal there is a partial averaging out of the contributions of the non-cubic parts of the crystalline electric field associated with different paramagnetic ions. But even so, such anisotropy as is left over can supply much information regarding the asymmetric part of the crystalline field and the influence on the magnetic properties (Krishnan and Mookherji, 1936).

In this communication the results of magnetic measurements on single crystals of salts of  $\text{Pr}^{+++}$  ions from room temperature down to liquid air temperature are discussed from the point of view of the splitting of the energy levels by the cubic as well as the non-cubic part of the field and ultimately of the magnetic behaviour of the ion.

#### EXPERIMENTAL

The experimental methods used in these measurements were the same as described in our previous paper (Mookherji, 1949) on cerium salts.

Specimens of praseodymium salts in these investigations were of high purity and were made available through the kindness of Professor Trombe of Paris University to whom we take this opportunity to express our thanks.

#### RESULTS

The results of measurements are collected in Tables I to IV. The same notations and diamagnetic corrections as adopted in the previous paper (Mookherji, 1949) are used in the present communication. Figs. 1 to 5 show the nature of variation of magnetic anisotropy and square of principle moments with temperature.

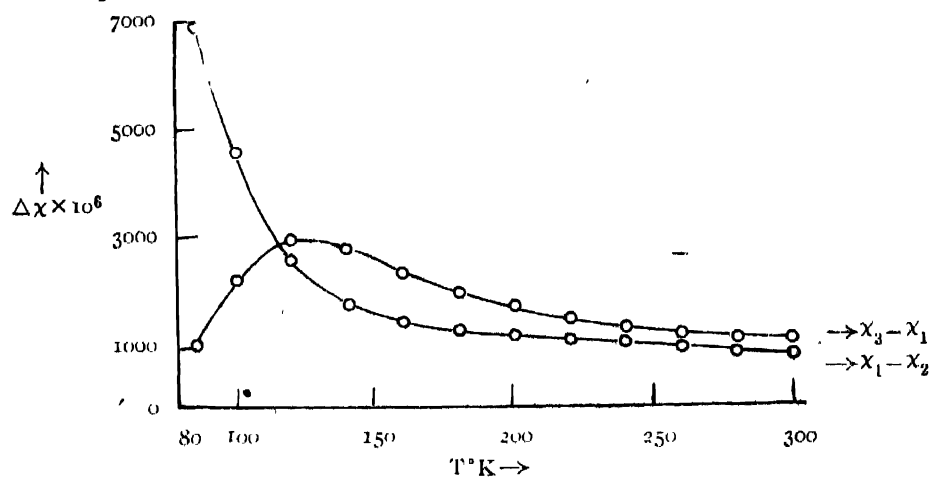


Fig. 1  
 $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

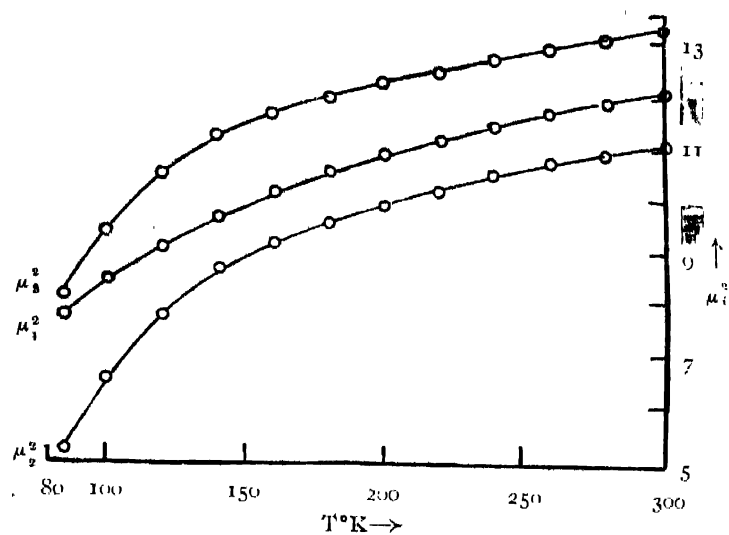


Fig. 2  
 $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

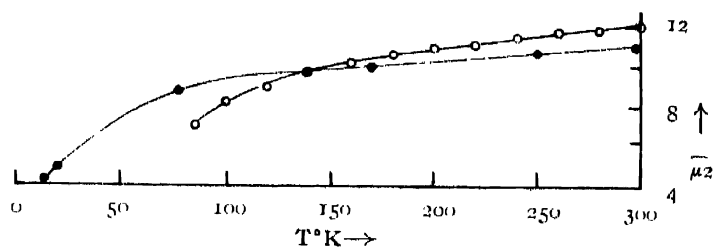


Fig. 3  
 $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$   
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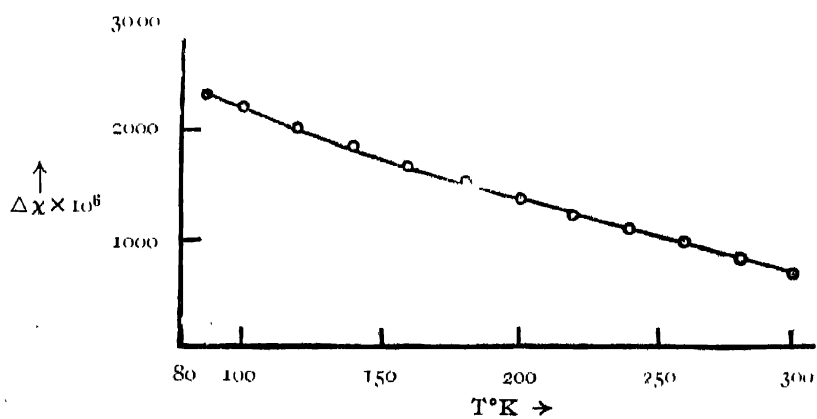


Fig. 4  
 $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

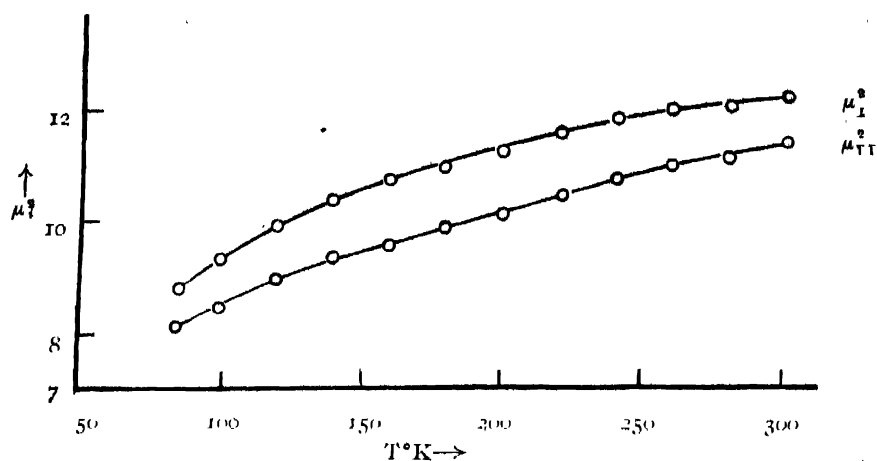


Fig. 5  
 $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{19} \cdot 24\text{H}_2\text{O}$

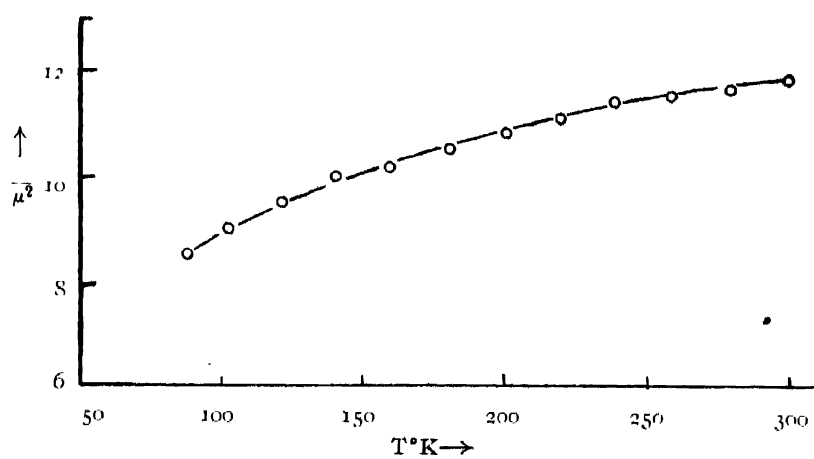


Fig. 5a  
 $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

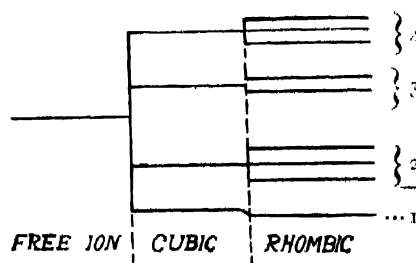


Fig. 6

#### THE MEAN MAGNETIC MOMENT AND THE CUBIC PART OF THE FIELD

The ground state of the  $\text{Pr}^{4++}$  ion is  $^3\text{H}_4$ . The next higher level namely the  $^3\text{H}_3$  is removed by about  $2100\text{ cm}^{-1}$  and hence at all ordinary temperatures

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the influence of the latter level on the magnetic behaviour of the ion will be negligible. The splitting of the ground level of  $\text{Pr}^{+++}$  ion under electric fields is given in Fig. 6 above.

TABLE I  
Magnetic anisotropy at 30°C.

Crystal	Crystallographic data	Mode of suspension.	Orientation in the field.	$\Delta\chi$	Magnetic Anisotropy
$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	Monoclinic prism $a:b:c$ 2.986:1:1.99 $\beta = 118^\circ$	'b' axis } vertical } 'a' axis } vertical } (001) plane } horizontal }	$\theta = +2^\circ.1$	795	$\begin{cases} \chi_1 - \chi_2 = 795 \\ \chi_3 - \chi_1 = 1005 \\ \psi = +25^\circ.9 \\ \text{Cal. } \psi = +26^\circ.0 \end{cases}$
			'b' axis } along field }	1006	
			'b' axis } along field }	1800	
$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	Trigonal	Trigonal axis horizontal	Trig. axis normal to field.	636	$\chi_{\perp} - \chi_{\parallel} = 636$

TABLE II  
Absolute susceptibility along a convenient direction

Crystal	Direction along which susceptibility was measured.	Temp. °C.	Density of the crystal	Volume susceptibility.	Corresponding gm. mol. susceptibility.	Corresponding gm. mol. susceptibility at 30°C.
$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	Along $\chi_1$ -axis	28.5	2.837	38.47	9,680	9,640
$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	Normal to Trigonal axis	30.5	2.182	13.49	9,430	9,450

We have already mentioned that the mean of the three principal susceptibilities is determined to a close approximation by the cubic part of the field alone. Taking the cubic part of the field  $b$  to be of the fourth order, the energy levels will be given by (Penney and Schlapp, 1932) the following equation (1)

$$\begin{aligned}
 W_1 &= 672a \\
 W_2 &= W_3 = W_4 = 336a \\
 W_5 &= W_6 = 96a \\
 W_7 &= W_8 = W_9 = -624a
 \end{aligned}
 \tag{1}$$

and the corresponding energy separations are 0,  $-336a$ ,  $-576a$  and  $-1296a$ , where ' $a$ ' is a constant determined by the magnitude of the cubic field, the

TABLE III

Temperature variation of Magnetic Anisotropy

Crystal	Temp. °K	Suspension used for measurement		$\chi_1 - \chi_2$	$\theta$
		'b' axis vertical	'a' axis vertical		
		$\chi_1 - \chi_2$	$\chi_3 - \chi_1 \cos^2\theta - \chi_2 \sin^2\theta$		
$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	300	800	1010	1010	+2.1
	280	868	1070	1070	2.1
	260	937	1170	1170	2.5
	240	1010	1320	1310	4.0
	220	1100	1500	1480	6.7
	200	1200	1780	1720	12.5
	180	1320	2120	1970	19.5
	160	1480	2670	2340	28.0
	140	1740	3460	2770	32.0
	120	2620	4590	2960	52.0
	100	4590	5710	2250	60.2
	85	6880	6750	1060	62.5
$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	Trigonal axis horizontal				
		$\chi_{\perp} - \chi_{\parallel}$			
	300	660			
	280	802			
	260	949			
	240	1080			
	220	1220			
	200	1380			
	180	1520			
	160	1690			
	140	1860			
	120	2020			
	100	2210			
	85	2340			

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TABLE IV

Temperature variation of principal susceptibilities

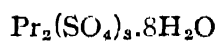
Crystal and direction along which measurement was taken	Temp. °K	$\chi'_1$	$\chi'_2$	$\chi'_3$	$\bar{\chi}'$	$\mu^a_1$	$\mu^a_2$	$\mu^a_3$	$\bar{\mu}^a$
$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ Along $\chi_1$ -axis	300	9960	9160	10970	10030	12.05	11.08	13.27	12.13
	280	10500	9630	11570	10570	11.82	10.87	13.06	11.92
	260	11140	10290	12300	11240	11.67	10.70	12.89	11.78
	240	11770	10760	13080	11870	11.39	10.42	12.66	11.49
	220	12470	11370	13960	12500	11.06	10.09	12.38	11.18
	200	13390	12190	15110	13560	10.80	9.830	12.18	10.90
	180	14380	13060	16350	14600	10.43	9.482	11.87	10.59
	160	15530	14050	17870	15800	10.02	9.070	11.53	10.21
	140	16900	15160	19670	17280	9.540	8.560	11.10	9.730
	120	18510	15890	21460	18690	8.960	7.681	10.39	9.010
$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ Along $\chi_{\perp}$ -axis	100	20360	16000	22870	19830	8.330	6.450	9.23	8.003
	85	22360	15480	22420	20420	7.66	5.137	8.03	7.00
	300	$\chi'_{\perp}$	$\chi'_{\parallel}$	$\bar{\chi}'$	$\mu^a_{\perp}$	$\mu^a_{\parallel}$	$\bar{\mu}^a$		
	280	10110	9450	9890	12.23	11.43	11.96		
	260	10610	9810	10340	11.98	11.08	11.68		
	240	11390	10440	11080	11.91	10.04	11.61		
	220	12190	11110	11830	11.80	10.75	11.45		
	200	12970	11750	12570	11.50	10.42	11.14		
	180	13830	12450	13370	11.15	10.04	10.78		
	160	15040	15520	14540	10.91	9.810	10.54		
$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ Along $\chi_{\perp}$ -axis	140	16550	14860	15990	10.68	9.585	10.32		
	120	18400	16540	17780	10.39	9.337	10.04		
	100	20550	18530	19880	9.920	8.964	9.000		
	85	23090	20880	22350	9.310	8.420	9.010		
	300	25900	23560	33750	8.880	8.076	8.610		

mean of the three principal susceptibilities will then be given by

$$\bar{\chi} = \frac{2Ng^2\beta^2}{a} [(.0092e^{13\nu} + .0333e^{-2\nu} - .0227e^{-7\nu} - .0199e^{-14\nu}) + (.1302e^{13\nu} + .0052e^{-7\nu})] \div [3e^{13\nu} + 2e^{-2\nu} + 3e^{-7\nu} + e^{-14\nu}] \quad (2)$$

Where  $\nu = \frac{48a}{kT}$ , and hence conversely from the observed mean of the three principal susceptibilities at any given temperature we can calculate the field constant. It is gratifying that over the whole of the temperature range studied by us, the observed magnetic data for the mean susceptibility fit well with the value  $a = -.585 \text{ cm}^{-1}$ . The observed values of  $\bar{\mu}^2$  and those calculated on the assumption of a cubic field of the fourth order with  $a = -.585 \text{ cm}^{-1}$  are given in Table V.

TABLE V



$$a = -.585 \text{ cm}^{-1}$$

Temp. °K	$\mu^2$	
	Calculated	Observed
300	11.74	12.1
200	10.86	10.9
100	8.19	8.01
85	7.18	7.0

The corresponding values for the  $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$  are given in Table VI.

TABLE VI



$$a = -.508 \text{ cm}^{-1}$$

Temp. °K	$\bar{\mu}^2$	
	Calculated	Observed
300	11.95	11.96
200	10.85	10.78
100	8.89	9.01
85	8.05	8.62



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Thus the magnetic data for the mean susceptibility for both the crystals can be satisfactorily explained on the basis of a suitable cubic field. The magnitudes of the cubic field required for this purpose are reasonable since they will correspond to an overall separation of  $756\text{ cm}^{-1}$  in the sulphate and  $661\text{ cm}^{-1}$  in the double nitrate. These are of the order of separation in the absorption spectra.

For the octahydrated sulphate data for the mean susceptibility at low temperature are available from the measurements of Görter and de Haas (1931). Their values are given in Table VII, for comparison

TABLE VII

Temp. °K	288	249.3	169.6	137.9	77.53	20.4	1.4.39
$\mu^2$	11.03	10.83	10.1	9.66	8.72	4.8	4.24

Among the other praseodymium salts for which magnetic data at low temperatures are available are :—

- (1)  $\text{Pr}_2(\text{C}_2\text{H}_5\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$ .....Faraday rotation of this crystal has been studied by Becquerel (1936).
- (2) The anhydrous sulphate whose mean susceptibility in the powder state has been measured by Görter and de Haas (1931).

In both these salts the temperature variation of  $\bar{\mu}^2$  is nearly the same as in the hydrated sulphate, which point to a crystalline field of nearly the same magnitude in all of them. This is to be expected since in all of them the field is presumably due to an octahedron of six negatively charged oxygen atoms, surrounding the  $\text{Pr}^{+++}$  ion, belonging to the water molecules in one case and to  $\text{SO}_4^{--4}$  groups in the other; but their distances from the ion will be nearly the same in both the cases.

We have seen that the cubic part of the field determines to a first approximation the mean square moment  $\bar{\mu}^2$ , i.e., its deviation from the free ion value of 12.81, of Hund, and that the rhombic part will have very little effect on  $\bar{\mu}^2$ , though the whole of observed anisotropy is due to it.

In the above discussions we have for simplicity taken the cubic field to be of the fourth degree. This is justifiable at least in the case of  $\text{Ce}^{+++}$  ion (Mookherji, 1949). In  $\text{Pr}^{+++}$  ions also the sixth degree terms of the cubic field, of any reasonable magnitude that may be present will not much affect the mean magnetic moment. This can be seen from the following Table VIII taken from a paper by Kynch (1937) which gives the energy levels under a cubic field involving respectively (1) the fourth degree terms only, (2) the fourth and sixth degree terms, the magnitudes of these two groups being chosen on the basis of the known distance of the negatively charged atoms surrounding the ion in the crystal.

TABLE VIII

Only Fourth degree terms	$\alpha,$	101.8	174.5	392.7	$\text{cm}^{-1}$
Sixth degree terms also included	$\alpha,$	116.7	200	403.3	

It will be seen that the two sets of values are not very different, showing that the effect of the sixth degree terms on the energy levels and hence on the magnetic moment is quite small.

It is observed that  $\lambda_1$  - axis of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  rotates through about  $63^\circ$  as the temperature is lowered from 300 to 85 degrees Kelvin.

#### MAGNETIC ANISOTROPY AND RHOHOMBIC PART OF THE FIELD

Though the rhombic part of the field does not to a first approximation affect the mean susceptibility, it is the rhombic that is responsible for the observed anisotropy of the crystal, and from the known anisotropy it should be possible with suitable simplifying assumptions to estimate the rhombic part. The assumptions referred to are :—

- (1) The principal axes of the rhombic field coincide with those of the cubic field
- (2) The field axes associated with different paramagnetic ions in the unit cell are all oriented parallel to one another.
- (3) That the rhombic terms which can be put in the usual form

$$V_r = Ax^2 + By^2 - (A+B)z^2 \quad (3)$$

have either

- (a) Some symmetry, corresponding, say to the two constants  $A$  and  $B$  being equal in which case the expression for  $V_r$  reduces to

$$V_r = A(x^2 + y^2 - 2z^2) \quad (4)$$

Or

- (b) Extreme asymmetry, corresponding to the coefficient of  $z^2$  being zero, in which case the expression for  $V_r$  reduces to

$$V_r = A(x^2 - y^2) \quad (5)$$

We shall refer to these two alternatives as case (a) and case (b) respectively.

With these assumptions, as Penney and Kynch (1939) have shown, the separations of the energy levels produced by the rhombic field will be as given in Fig. 7

Case (a)—Denoting by numbers 1 to 4, the four split levels split by the cubic part of the field as shown in Fig. 7, the overall splitting produced by

the rhombic part will be  $28m$  for level (2) and  $8m$  for level (4), where  $m$  is

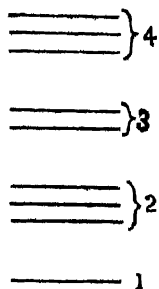


FIG. 7

a constant determined by the rhombic field. The corresponding expressions for the principal susceptibilities at room temperature will be

$$\left. \begin{aligned} \mu_x^2 &= \mu_y^2 = 12.14 + .058m \\ \mu_z^2 &= 12.14 - .116m \end{aligned} \right\} \quad (6)$$

Case (b)—Here the overall separations of (2) and (4) will be  $28m$  and  $8m$  respectively. The susceptibility at room temperature is given by

$$\left. \begin{aligned} \mu_x^2 &= 12.14 + .058m \\ \mu_y^2 &= 12.14 - .058m \\ \mu_z^2 &= 12.14 \end{aligned} \right\} \quad (7)$$

12.14 represents the mean susceptibility of the crystal at room temperature. It is independent of  $m$  and is determined by the cubic field alone.

In actual crystals the simplifying assumptions (1) to (3) will not hold at all. But the order of magnitude of the rhombic part of the field can still be estimated roughly.

From equations (6) and (7) it will be seen that  $\Delta\mu^2$  is equal to  $0.174m$  in case of (a) and equal to  $0.116m$  in case of (b). In both cases the separations are equal to  $28m$  and  $8m$  respectively for levels (2) and (4). For any rhombic field in general, we may calculate the order of magnitude of the separations by taking  $\Delta\mu^2$  to be of the order of  $0.15m$ , and the separations to be of the order of  $10m$ . Now in  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ,  $\bar{\mu}^2$  is about  $12 \text{ cm}^{-1}$  and the anisotropy  $\frac{\Delta\mu^2}{\bar{\mu}^2}$  is about 0.2 from which we obtain  $\Delta\mu^2 = 2.5 \text{ cm}^{-1}$ . Since

$\Delta\mu^2 \sim 0.15m$ , this gives  $m \sim 0.16 \text{ cm}^{-1}$ , and the separation produced by the rhombic field, which we have taken to be of the order  $10m$ , should be about  $160 \text{ cm}^{-1}$ . This is not much smaller than the separations by the cubic part of the field.

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